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ANNUAL REPORT

GERMANIUM

By Thomas O. Llewellyn

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GERMANIUM

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Secretary

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MINES

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Director

October 1991

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COVER PHOTO:
The U.S. Army AH-64 Apache *attack helicopter employs a thermal imaging infrared system. The germanium-containing lenses and windows of the system transmit thermal radiation similar to the way optical glass transmits visible light. This enables the pilot to fly the helicopter as low as a few feet above ground and also to detect armored targets at night. (Photo is courtesy of Hughes Aircraft. The photo was released by the Department of Defense.)*

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GERMANIUM

By Thomas O. Llewellyn

Mr. Thomas O. Llewellyn is a physical scientist with the Branch of Industrial Minerals. He has covered germanium for 4 years. Domestic survey data prepared by Tony E. Morris, mineral data assistant.

Domestic production and consumption of refined germanium were estimated at lower levels than those of 1989. The declines in germanium production and consumption were attributed to an existing oversupply of metal and to a lower demand from the military sector. Infrared systems and fiber optics continued to be the major end uses.

DOMESTIC DATA COVERAGE

Refinery production and consumption data for germanium are estimated by the U.S. Bureau of Mines based on discussions with domestic producers.

BACKGROUND

Germanium is recovered as a minor byproduct of the refining of base metal ores, and the potential supply of this metal, which is dependent on the level of zinc production, has historically exceeded demand.

Invention and development of the germanium transistor opened the path for the solid-state electronic field and, from 1950 through the early 1970's, provided an excellent market for germanium. Despite the continued growth of the electronics industry in the 1970's, germanium demand for transistors, diodes, and rectifiers declined because germanium was being replaced by electronic-grade silicon. However, the reduced demand for germanium in the electronics field was offset by a dramatic increase in demand for germanium in both infrared night vision systems and fiber-optic communication networks.

Definition, Grades, and Specifications

Germanium has a metallic appearance, grayish white in color, and lustrous, hard, and very brittle. It is a semiconductor, with electrical properties between those of a metal and an insulator. The National Stockpile Purchase Specification P-114-R, December 16, 1989, for intrinsic germanium metal specifies an electrical resistivity of 50 ohm-centimeters at 20° C (40 ohm-centimeters at 25° C) over the entire ingot length.

Germanium is available commercially as a tetrachloride and high-purity oxide and in the form of zone-refined ingots, single-crystal bars, castings, doped semiconductors, optical materials, optical blanks, and other specialty products.

Industry Structure

Most germanium occurs as a minor constituent of certain base metal ores and coal deposits. Those producers that currently recover primary germanium for the most part depend on germanium-rich residues, mainly from zinc derived from past or present base metal smelting operations.

In the United States, Eagle-Picher Industries Inc.'s Quapaw, OK, Specialty Materials Div. has the capability of recovering primary germanium from zinc smelter residues. Eagle-Picher also reprocessed scrap. Kawecki Berylco Industries Inc., a division of Cabot Corp. in Revere, PA, and Atomergic Chemetals Co., Plainview, NY, produced germanium from reprocessed scrap and semirefined foreign material.

The Jersey Miniere Zinc Co. in Clarksville, TN, continued to produce germanium-rich residues as a byproduct of processing zinc ores from its Gordonville and Elmwood Mines. These residues were shipped to Metallurgie Hoboken Overpelt S.A. (MHO) in Belgium for germanium recovery and refining.

Little information was available on the financial structure of U.S. and world germanium industries. Germanium refiners usually were involved in the production and sale of many different metals and specialty products.

Resources

Minerals in which germanium is concentrated are germanite, a sulfoarsenite of copper, germanium, and iron with an average content of 5% germanium; argyrodite, a double sulfide of germanium and silver containing 5% to 7% germanium; renierite, a complex sulfide of arsenic, copper, germanium, iron, tin and zinc with 6% to 8% germanium; and several other minerals such as canfieldite, itoite, stottite, and ultrabasite. Primary germanium minerals are normally formed in sulfide mineralization processes at low-to-intermediate temperatures, and secondary varieties may result from supergene alteration of sulfide ore deposits.[1]

Currently, there are two major reserves of germanium in the United States. The largest is the recoverable germanium that occurs as a minor constituent of zinc sulfide ores in the middle Tennessee zinc district. The other major reserve of germanium is in southern Utah. Here the germanium is found in the iron oxide ore zone of a depleted copper mine.

There are no reliable germanium assay data available for many areas of the world. The U.S. and world resources could be expanded if germanium were to be recovered from ash and flue dusts resulting from burning of certain coals for power generation.

Technology

Germanium is obtained commercially as a byproduct of base metal refining and extracting. Improvements have been made, but the basic processes have remained virtually unchanged.

Regardless of the source, germanium raw materials are reacted with concentrated hydrochloric acid to form germanium tetrachloride, which is then purified by fractional distillation. The purified germanium tetrachloride is hydrolyzed with water to produce germanium dioxide, which is removed by filtration and dried. Dried germanium dioxide is reduced with

hydrogen at about 760° C to a germanium metal powder, which is then melted and cast into metal bars. These bars are then zone-refined to produce intrinsic-grade metal. This high-purity metal is mainly used for electronic and infrared optics. Zone refining produces polycrystalline germanium.[2]

Certain applications of germanium, such as gamma-ray detectors, require single-crystal germanium. Single crystals are produced by two methods, the horizontal pulling process or the vertical pulling process, also known as the Czochralski method.

More than 50% of the metal used during the manufacture of most electronic and optical devices is recycled as new scrap. As a result of the low unit use of germanium in microelectronic devices, very little germanium returns as old scrap.

Substitutes

Less-expensive silicon substitutes for germanium in certain electronic applications. Certain bimetallic compounds of gallium, indium, selenium, and tellurium can also substitute for germanium. Germanium is more reliable in some high-frequency and high-power applications and more economical as a substrate for some light-emitting diode applications. In infrared guidance systems, zinc selenide or germanium glass substitutes for germanium metal, but at the expense of performance.

Economic Factors

Table 1 shows import duties for germanium products, which became effective on January 1, 1989, under the new Harmonized Tariff Schedule of the United States. Domestic producers are granted a depletion allowance of 14% on both domestic and foreign production of germanium.

Operating Factors

Germanium has little or no effect upon the environment because it usually occurs only as a trace element in some ores and carbonaceous materials. The small quantities used in commercial applications also pose no threat to the environment. Germanium compounds generally have a low order of toxicity, except for germanium tetrahydride, which is considered toxic.

Based on a 1976 report, the energy requirements for the production of zone-refined germanium metal from zinc sulfide concentrates and scrap is 2,145 million British thermal units per net ton of germanium ingot.[3]

TABLE 1

U.S. IMPORT DUTIES FOR GERMANIUM MATERIALS

Item	HTS No.	Most favored nation (MFN) Jan. 1, 1990	Non-MFN Jan. 1, 1990
Germanium: Waste and scrap	8112.30.3000	Free	Free.
Germanium other: Unwrought	8112.30.6000	3.7% ad valorem	25% ad valorem.
Germanium other: Other	8112.30.9000	5.5% ad valorem	45% ad valorem.

ANNUAL REVIEW

Strategic Considerations

The importance of germanium as a strategic and critical material was determined by the Federal Emergency Management Agency, and, on July 6, 1984, it was included in the National Defense Stockpile (NDS) with an initial goal of 30,000 kilograms of germanium metal. On July 24, 1987, a new NDS goal of 146,000 kilograms was established, based on the Army's estimates for actual emergency conditions of mobilization.

Some of the metal inventory acquisitions made the previous year were delivered in 1990, and, as of December 31, the stockpile inventory was 58,287 kilograms of germanium metal.

Production

The U.S. Bureau of Mines estimated domestic refinery production from both primary and secondary materials to be 18,000 kilograms, a decrease of 10% compared with that of 1989.

In August, Hecla Mining Co., the owner of the only known mine and refinery in the world where germanium and gallium were recovered as principal products, closed the mine and refinery about 6 months after it reopened. The operation, near St. George, UT, had a production capacity of 20 metric tons per year of germanium and 7 metric tons per year of gallium. Most of the mined ore was stockpiled because of technical difficulties in the processing plant. The company expected to resume operations pending processing improvements and higher price quotations for the metal.

Consumption and Uses

The U.S. Bureau of Mines estimated that consumption of germanium decreased about 5.5% compared with the level of 1989. The estimated consumption pattern by end use of germanium in 1990 was as follows: infrared systems, 60%; fiber optics, 8%; gamma-ray, X-ray, and infrared detectors, 9%; semiconductors (including transistors, diodes, and rectifiers), 10%; and other applications (catalysts, phosphors, metallurgy, and chemotherapy), 13%.

Infrared systems continued to be the major end use for germanium. Infrared optics were mainly used for military guidance and weapon-sighting systems. Germanium-containing lenses and windows transmit thermal radiation similar to visible light transmission by optical glass. Germanium glass also was used for nonmilitary surveillance and monitoring systems in fields such as satellite systems and fire alarms. Germanium was used as a dopant in the core of many optical fibers employed in telecommunications.

Martin Marietta Corp. was applying a new transparent hard carbon coating to the night vision system windows of the *Apache* attack helicopter. The night vision system enables pilots to fly the helicopter a few feet above ground in darkness, operate under low-weather-visibility conditions, and detect tanks or other armored targets at night. The system's germanium optical windows were abraded by exposure to sand and dust, which affected the clarity of the television-like infrared picture. The carbon coating protection was designed to last more than 20 years compared to about 3 years achieved by the previously used thorium fluoride coating. The U.S. Army's expected savings on maintenance and spare parts cost on night

vision systems were estimated to be about $28 million during 3 years.[4]

Markets and Prices

Throughout 1990, domestic producer prices for germanium metal and dioxide, published by Metals Week, remained at the levels established in late 1981 of $1,060 and $660 per kilogram, respectively. However, discounting by producers was evident during 1990 because of competition from imported materials.

The Belgian producer's price for germanium metal, published by Metal Bulletin (London), remained at about $802 per kilogram throughout the year.[5]

Foreign Trade

In 1990, the estimated germanium content of imports was approximately 50,000 kilograms. Total imports of germanium materials increased significantly compared with those of 1989. France, Belgium, Canada, and the United Kingdom, in descending order of shipments, accounted for approximately 80% of the total U.S. germanium imports for 1990.

World Review

World refinery production was estimated at 76,000 kilograms, a decrease of about 7% compared with the 1989 level. The decline in world production was attributed to an oversupply and to a lower level of demand for the metal. Primary germanium was produced by MHO, Belgium; Johnson Matthey Electronics, Canada; Societe Miniere et Metallurgique de Penarroya S.A., France; Otavi Minon AG and Preussag AG, the Federal Republic of Germany; Pertusola Sud SpA, Italy; and Nippon Denshi Kinzoku and Sumitomo Metal Mining Co. Ltd., Japan. Germanium refineries also were in China and the U.S.S.R.

Capacity.—The data in table 3 represent rated annual production capacity for refineries on December 31, 1990. Rated capacity was defined as the maximum quantity of product that can be produced in a period of time on a normally sustainable, long-term operating rate, based on the physical equipment of the plant and routine operating procedures for labor, energy, materials, and maintenance.

TABLE 3

WORLD ANNUAL GERMANIUM REFINERY PRODUCTION CAPACITY, DECEMBER 31, 1990

(Thousand kilograms)

	Capacity
North America:	
Canada	10
United States	60
Total	70
Europe:	
Belgium	50
Centrally planned economy countries	40
Other	65
Total	155
Asia:	
China	10
Japan	35
Total	45
World total	270

Capacity includes both operating plants and plants temporarily closed that, in the judgment of the author, can be brought into production within a short period of time with minimum capital expenditures.

Rated capacities of germanium refineries were estimated based on discussions with some officials from private industry, past and present production rates, and published capacity data.

Japan.—Germanium metal production was 3,368 kilograms, which was at about the same level as in 1989. Dioxide production decreased from 13,302 kilograms in 1989 to 12,350 kilograms in 1990.[6]

Spain.—Telefonica S.A., the state-owned telephone company, is turning to optical fibers to improve its telecommunications system. It has already installed about 12,000 kilometers of fiber optic cable, and an additional 21,000 kilometers of cable are expected to be installed before the end of 1993.[7]

United Kingdom.—British Telecom, London, will supply and install the first fiber-optic cable link in Vietnam. A 460-kilometer network system will connect Ho Chi Minh City with Nha Trang at an estimated cost of $6.3 million.[8]

TABLE 2

U.S. IMPORTS OF GERMANIUM MATERIALS, BY COUNTRY[1]

Country	1989		1990	
	Gross weight (kilograms)	Value	Gross weight (kilograms)	Value
Belgium	15,985	$12,027,567	7,486	$7,611,049
Canada	2,407	1,470,524	5,469	2,841,950
China	3,195	1,607,868	2,078	655,351
France	7,973	5,313,134	21,087	12,709,770
Germany, Federal Republic of	3,421	1,145,407	2,992	1,088,355
Hong Kong	16	6,480	3,062	1,302,963
Israel	55	35,221	508	89,247
Japan	8	3,034	30	3,210
Netherlands	849	281,574	4	4,697
Singapore	15	8,503	16	5,000
Spain	—	—	1,346	243,184
Sweden	—	—	20	27,964
Switzerland	3,260	182,166	—	—
U.S.S.R.	—	—	307	121,321
United Kingdom	2,921	1,707,877	5,364	1,263,694
Total	40,105	23,789,355	49,769	27,967,755

[1]Unwrought and waste and scrap.

Source: Bureau of the Census.

Current Research

A new fiber-optic lighting system for automobiles was being developed by the Advanced Technology Department of General Electric Lighting. This system uses less power than two of today's halogen headlights, while providing the same amount of light. It has a potential application of replacing as many as 80 light sources now used in cars. Furthermore, the fiber system does not require conventional wiring nor light bulbs, and its small size (about 1 inch high) should allow car designers to taper the front end of the car to achieve a more aerodynamic curvature.[9]

The Roskill organization issued its 1990 germanium report. This comprehensive report discussed and analyzed world production of germanium by country and individual company. It also contained information on end-use markets, international trade patterns, and trends in prices.[10]

OUTLOOK

There were abundant supplies of germanium materials on the market in 1990. Germanium supplies are likely to remain high for the next 2 to 4 years because of an increased availability of concentrates from Canada and a considerable amount of germanium metal emerging into the world market from the U.S.S.R. For the second consecutive year, producers were forced to lower prices to maintain their share of the market.

Market analysts agree that all primary germanium producers will probably face difficult times in the near future. This assessment is based on a continuing global oversupply of germanium materials together with a low market demand.

[1]Weber, J. N. Geochemistry of Germanium. Dowden, Hutchison & Rose Inc., Strudosburg, PA, 1973, pp. 1–5.

[2]Adams, J. H. Germanium Compounds. Ch. in Encyclopedia of Chemical Technology. Kirk-Othmer, 3d ed., v. 11, 1983, pp. 791–802.

[3]Battelle Columbus Laboratories. Energy Use Patterns in Metallurgical and Nonmetallurgical Mineral Processing (Phase 6-Energy Data and Flowsheet, Low-Priority Commodities). BuMines OFR 117(1)-76, 1976, pp. 79-82; NTIS PB 261150/AS.

[4]Newly Developed Optical Coating Expected To Save Army $27.9 Million Over 3 Years. Martin Marietta Corp. Press release, Orlando, FL, Jan. 1990.

[5]Where necessary, values have been converted from Belgian francs (BF) to U.S. dollars at the average exchange rate of BF37.0 = US$1.00.

[6]Japan Metal Journal. V. 21, No. 11, Mar. 18, 1991, pp. 7–8.

[7]Photonics Spectra. Spain Looks to Fiber To Update Network. V. 24, No. 3. Mar. 1990, p. 118.

[8]Laser Focus World. Fiberoptics Industry Report. V. 26, No.1, Jan. 1990, p. 162.

[9]Waggoner, J. Accent on Applications—GE Light Engine Illuminates Autos. Photonics Spectra, v. 24, No. 11, Nov. 1990, p. 16.

[10]Roskill Information Services Ltd. The Economics of Germanium 1990. London, England, 7th ed., Apr. 1990, 175 pp. and Appendices A and B.

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